

Preliminary communication

The 1,4-addition of *n*-butyllithium to 2-ferrocenylquinoline

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SUMMARY

Treatment of 2-ferrocenylquinoline with *n*-butyllithium gave 1,4- rather than the expected 1,2- addition across the quinoline.

Although it is well documented¹ that alkyllithiums add preferentially to quinolines across the 1,2-position, it has been claimed that 1,4-addition occurred in the treatment of 4-methylquinoline with *n*-butyllithium and phenyllithium². Reinvestigation of this report confirmed that 1,2- and not 1,4-addition had occurred^{3,4}.

We now offer conclusive evidence for 1,4-addition in the reaction between 2-ferrocenylquinoline (I) and *n*-butyllithium. The product obtained, 1,2-dihydro-2-ferrocenyl-4-*n*-butylquinoline (III), was formed presumably from the intermediate (II) by a 4,2-hydrogen shift. Such rearrangements are well authenticated in strongly basic media⁵. The dihydroquinoline (III) was aromatised on stirring with manganese dioxide in chloroform⁶. Microanalysis, infrared and in particular the PMR absorption spectra confirmed the aromatic character of the quinoline (V) and the site of butylation as C(4). Table 1 compares the PMR spectra of quinoline, 2-ferrocenylquinoline and 2-ferrocenyl-4-butylquinoline in benzene and carbon tetrachloride. Comparison of the chemical shifts and the solvent shifts ($\Delta_{\text{C}_6\text{D}_6}^{\text{CCl}_4}$) within Table 1 and with the values for other substituted quinolines^{7,8} supported the structure of the quinoline (V). The product of 1,2-addition (IV) could not have aromatised with manganese dioxide nor would it have given the PMR spectrum detailed in Table 1.

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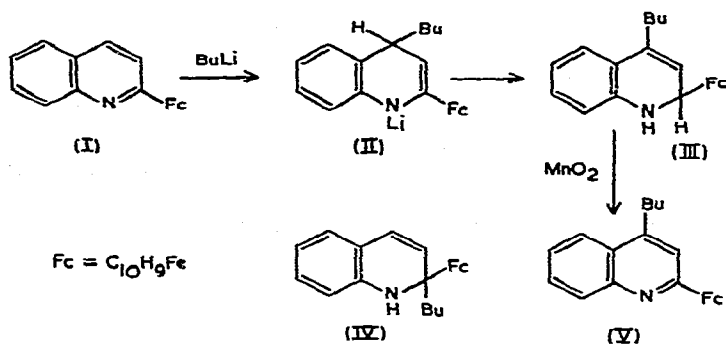


TABLE 1

SOLVENT EFFECTS IN THE PMR SPECTRA^a OF SUBSTITUTED QUINOLINES

Proton	2-Ferrocenyl-4-butylquinoline			2-Ferrocenylquinoline			Quinoline
	CCl ₄ (ppm)	C ₆ D ₆ (ppm)	$\Delta_{C_6D_6}^{CCl_4}$	CCl ₄ (ppm)	C ₆ D ₆ (ppm)	$\Delta_{C_6D_6}^{CCl_4}$	
H ₂	—	—	—	—	—	—	0.06
H ₃	7.88s	7.56s	0.32	7.54	7.24d	0.30	0.52
H ₄	—	—	—	8.00d	7.62d	0.38	0.59
H ₅ , H ₆ , H ₇	7.3–7.8m	7.1–7.5m	—	7.3–7.8m	7.1–7.5m	—	—
H ₈	8.06d	8.28d	-0.22	8.08d	8.28d	-0.20	-0.24

^a Spectra were recorded in 0.2 M solution at 100 MHz with TMS as internal standard.

The PMR results for the dihydroquinoline (III) collected in Table 2 show coupling between the hydrogen atoms on C(1) and C(2) ($J_{1,2} = 2$ Hz). After shaking the sample with deuterium oxide to exchange the hydrogen on C(1) for deuterium no resonance was observed at δ 3.61 ppm and the double doublet at δ 5.28 collapsed to a doublet ($J_{2,3} = 10$ Hz).

TABLE 2

PMR SPECTRUM^a OF THE DIHYDROQUINOLINE (III) IN BENZENE

Proton	δ (ppm)	Coupling constant (Hz)
H ₁	3.61 s (broad)	—
H ₂	5.28 q	$J_{2,3} = 10; J_{1,2} = 2$
H ₃	6.21 d	$J_{2,3} = 10$
H ₅	6.85 d	$J_{5,6} = 7$
H ₆ or H ₇	6.96 t	—
H ₇ or H ₆	6.58 t	—
H ₈	6.21 d	$J_{7,8} = 8$

^a Spectra were recorded in 0.2 M solution at 100 MHz with TMS as internal standard.

These results can be interpreted only in terms of the structure (III) and it is probable that the strongly electron releasing character of the ferrocenyl group⁹ directs the butyl anion to the 4-position.

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